This section describes the field and laboratory methods used to conduct the Monitoring Program, which includes precipitation and flow monitoring, stormwater sampling, laboratory analyses, and river toxicity tests.

3.1 PRECIPITATION AND FLOW MEASUREMENT

3.1.1 Precipitation Monitoring

For every monitoring station, a minimum of one automatic tipping bucket (intensity measuring) rain gage is located nearby or within the tributary watershed. Large watersheds may require multiple rain gages to accurately characterize the rainfall. The Los Angeles County Department of Public Works operates various automatic rain gages throughout the county. Existing gages near the monitored watersheds are also utilized in calculating stormwater runoff and are essential to develop runoff characteristics for these watersheds.

3.1.2 Flow Monitoring

Flow monitoring equipment is needed to trigger the automated samplers because the Monitoring Program requires flow-weighted composites for many constituents. Flows are determined from measurements of water elevation as described below.

The water elevation in a storm drain is measured by the stage monitoring equipment, and the flow rate is derived from a previously established rating table for the site or calculated with an equation such as Manning's. The Los Angeles County Department of Public Works uses rating tables generated from analysis of storm drain cross sections and upstream/downstream flow characteristics. The rating tables are modified if it is demonstrated in the field through stream velocity measurements that calculated table values are incorrect. Previous stormwater flow measurement efforts indicates that all stations will require multiple storm events to gather the data necessary for calibration of the measurement devices.

The automatic samplers utilize pressure transducers as the stage measurement device. However, pressure transducers are only accurate as flow measurement devices in open channel flow regimes. Therefore, for stations monitoring flows in underground storm drains, efforts were made to select drains that do not surcharge (flow under pressure) during events smaller than a 10-year storm event.

3.2 STORMWATER SAMPLING

3.2.1 Sample Collection Methods

Grab and composite sample collection methods, defined below, were used during the 1998-99 storm season.

- **Grab Sample** - a discrete, individual sample taken within a short period of time, usually less than 15 minutes. This method is used to collect samples for constituents that have very short holding times and specific collection or preservation needs. For example, samples for coliforms are taken directly into a sterile container to avoid non-resident bacterial contamination.

- **Composite Sample** - a mixed or combined sample created by combining a series of discrete samples (aliquots) of specific volume, collected at specific flow-volume intervals. Composite sampling is ideally conducted over the duration of the storm event.

During a storm event, grab samples were collected during the initial portion of the storm (on the rising limb of the hydrograph) and taken directly to the laboratory.

Flow composite storm samples were obtained using an automated sampler to collect samples at flow-paced intervals. Samples collected at each station were combined in the laboratory to create a single flow-weighted sample for analysis.

During the storm season, the sampler was programmed to start automatically when the water level in the channel or storm drain exceeded the maximum annual dry weather stage. A sample was collected each time a set volume of water had passed the monitoring point (this volume is referred to as the pacing volume or trigger volume). The sample was stored in glass containers within the refrigerated sampler. A minimum of eight liters of sample was required to conduct the necessary laboratory analyses for all the constituents. The automated sampler was deactivated by field personnel when the water level in the channel or storm drain fell to about 120 percent of the observed maximum annual dry weather flow stage.

Samples were retrieved from the automated samplers as soon as possible to meet laboratory analysis holding time requirements. As samples were collected, rainfall and runoff data were logged and stored for transfer to the office.

3.2.2 Field Quality Assurance/Quality Control Plan

Properly performed monitoring station set up, water sample collection, sample transport, and laboratory analyses are vital to the collection of accurate data. Quality Assurance/Quality Control (QA/QC) is an essential component of the monitoring program.

Evaluation of Analytes and QA/QC Specifications for Monitoring Program (Woodward-Clyde, 1996a) describes the procedures used for bottle labeling, chain-of-custody tracking, sampler equipment checkout and setup, sample collection, field blanks to assess field contamination, field duplicate samples, and transportation to the laboratory.

An important part of the QA/QC Plan is the continued education of all field personnel. Field personnel were adequately trained from the onset and informed about new information on stormwater sampling techniques on a continuing basis. Field personnel also evaluate the field activities required by the QA/QC Plan, and the Plan is updated if necessary.

Bottle Preparation

For each monitoring station, a minimum of three sets of bottles was available so that up to two complete bottle change-outs could be made for each storm event. Bottle labels contained the following information:

- LADPW Sample ID Number
- Station Number
- Station Name

- Sample Type (Grab or Composite)
- Laboratory Analysis Requested
- Date
- Time
- Preservative
- Temperature
- Sampler's Name

Bottles were cleaned at the laboratory prior to use, then they were labeled and stored in sets. Each station was provided with the same number, types, and volumes of bottles for each rotation unless special grab samples were required. Clean composite sample bottles were placed in the automated sampler when samples were collected. This practice ensured readiness for the next storm event. All bottles currently not in use were stored and later transported in plastic ice chests. Composite sample bottles were limited to a maximum of 2-1/2 gallons each, to ensure ease of handling.

Chain-of-Custody Procedure

Chain-of-custody forms were completed to ensure and document sample integrity. These procedures establish a written record which tracks sample possession from collection through analysis.

Field Setup Procedures

All field sampling locations were fixed sites, with the sampler placed on a public road or flood control right-of-way. After sample collection, field staff prepared the sampler for collection of the next set of samples either in storm mode or in dry weather mode. Inspection of visible hoses and cables was performed to ensure proper working conditions according to the site design. Inspection of the strainer, pressure transducer, and auxiliary pump was performed during daylight hours in nonstorm conditions.

The automated sampler was checked at the beginning of the storm (during grab sample collection) to ensure proper working condition and to see if flow composite samples were being collected properly. Dry weather collection techniques were similar, with grab and 24-hour composite samples being collected.

Bottles were collected after each event and packed with ice and foam insulation inside individually marked ice chests. Chain-of-custody forms were completed by field staff before transportation of the samples to the laboratory. Under no circumstance were samples removed from the ice chest during transportation from the field to the laboratory.

Travel Blanks and Field Duplicates

Potential field contamination was assessed through analysis of travel blanks and duplicate grab samples. Field travel blanks were collected for each monitoring station during every sampling event to quantify post sampling contamination. The monitoring program also included field

duplicates to assess the precision of laboratory results. A field duplicate, the origin of which was unknown to the laboratory, was collected for each sampling event. This methodology for assessing post sampling contamination and laboratory testing procedures provided data to measure the precision and accuracy of the laboratory results.

3.2.3 Sampling Frequency

During the 1998-99 storm season, the Permit required the Department to sample up to 200 "station events" for the land use sites. A station event is defined as collection of one sample at one station. The Municipal Permit specifies sampling at mass emission stations to total five events per year during dry weather, storm, or a combination of both.

3.3 LABORATORY ANALYSES

The Department of Agricultural Commissioner/Weights and Measures (ACWM) Environmental Toxicology Laboratory provides water quality laboratory and related services to the LACDPW. The ACWM lab is state certified to perform the water quality analyses contracted by LACDPW. The ACWM Lab maintains a laboratory analysis program that includes Quality Assurance and Quality Control protocols consistent with the objectives of the monitoring program required by the Permit (Section 3.3.3).

3.3.1 Possible Constituents of Concern

Possible constituents of concern for each element of the Monitoring Program are specified in the Municipal Permit. The constituents of concern for land use station monitoring are:

- Total Suspended Solids
- Total Nitrogen
- Total Phosphorus
- Cadmium
- Chromium
- Copper
- Lead
- Mercury
- Nickel
- Selenium
- Silver
- Zinc
- Chlordane
- Chlorpyrifos
- Diazinon
- Malathion
- Simazine
- Total DDT
- Total PAHs
- Total PCBs

Constituents of concern for mass emission monitoring include those listed above plus:

- Bacteria
- Total Phenols
- TPH
- Oil and Grease
- Cyanide

3.3.2 Analytical Suite and Analytical Methods

The suite of analytes and associated detection limits for samples collected at the land use stations and mass emission stations are specified in the Municipal Permit. Constituents of concern for derivation of event mean concentrations are also specified by the Permit. All the laboratory methods used for analysis of the stormwater samples are approved by the California Department of Health Services and are in conformance with USEPA approved methods.

Table 3-1 shows all the constituents monitored during the 1998-99 season, including constituents analyzed with composite or grab samples. The table lists the method number, the reporting limit, the data quality objectives, and other relevant information for each constituent. The table also shows which constituents were monitored at the land use sites versus the mass emission sites. Analyses of constituents in samples collected for the Critical Source/BMP Monitoring Study were performed using the same methods and reporting limits as those given in Table 3-1.

The laboratory made an effort to provide the lowest detection limits attainable without compromising the reliability of the data. "Detection limit" (DL) is defined by the USEPA as "the concentration above which we are 99% confident that the analyte is present at a concentration greater than zero" (40 CFR Part 136 Appendix B). For this project the laboratory made some allowance for interference in the analysis due to the complex nature of the sample matrix by performing a DL study using a water sample collected from a channel during dry weather. These 'matrix specific' DLs are the reported DLs in the data tables. Data below the DL are reported as zero. The Practical Quantitation Limit (PQL) is the concentration above which the analyte can be accurately quantified. Reported PQLs were developed by the laboratory during the analysis of stormwater runoff samples using professional judgment to account for matrix interferences. Data that fall between the DL and PQL are reported by the laboratory at the apparent concentrations. When reviewing these data it should be noted that the concentrations below the PQL are estimated.

3.3.3 Quality Assurance and Quality Control

The primary objective of the laboratory quality assurance/quality control program is to ensure that the analyses are scientifically valid, defensible, and of known precision and accuracy. The ACWM laboratory maintains quality assurance/quality control procedures (as described in their Quality Assurance Manual) in accordance with requirements of the California Department of Health Services. The ACWM laboratory standard operation procedures include method validation, equipment calibration, preventive maintenance, data validation procedures, assessment of accuracy and precision, corrective actions, and performance and system audits. The QA/QC review and data validation for the 1998-99 monitoring data was conducted by ACWM Lab, and the QA/QC documentation is available within the ACWM Lab files. The

validated data as provided by the ACWM Lab were used for data analysis and interpretation with no further QA/QC review.

3.4 RIVER TOXICITY TESTS

3.4.1 Dry Weather Methods

Sampling was conducted during dry weather flow conditions at the Los Angeles and San Gabriel Rivers. The San Gabriel River dry weather sample was a 24 hour, time weighted composite collected by autosampler on October 22, 1998. The Los Angeles River sample was a composite of 9 grabs collected manually by bucket over an 8 hour period between 0800 and 1600 on October 22, 1998. Sampling locations were LACDPW mass emission stations S-10 (Los Angeles River) and S-14 (San Gabriel River). Samples were stored under refrigeration until tested on October 23.

Toxicity was measured using the purple sea urchin fertilization test as described by Chapman et al. (1995). Sea urchin gametes were obtained from specimens collected from a relatively uncontaminated area in northern Santa Monica Bay. In the test, sea urchin sperm are exposed to various concentrations of the test sample for 20 minutes at a temperature of 15°C. Sea urchin eggs are then added to each sample and given 20 minutes for fertilization to occur. Preservative is then added to the samples, which are later examined with a microscope to determine the percentage of fertilized eggs.

Since the toxicity test uses a marine organism, the salinity of the river samples was adjusted to a typical seawater value by addition of hypersaline brine. Addition of the brine diluted the samples, restricting the highest concentration of sample tested to 50%. Additional test concentrations (25, 12, 6, 3, and 1.5%) were prepared by adding laboratory seawater (filtered natural seawater collected from offshore Redondo Beach) to the samples. A brine control was included in the experiment to check for toxicity introduced by the salinity adjustment procedure. The brine control consisted of deionized water, laboratory seawater, and brine at the same concentration found in the 50%and 25% river samples.

A reference toxicant test was conducted at the same time in order to document variability in test sensitivity. This test consisted of five concentrations of dissolved copper, ranging from 10 µg/L to 65 µg/L.

Water quality measurements (pH, dissolved oxygen, conductivity, and total ammonia) were made on the test samples at the beginning of the toxicity test. For the river samples, water quality was measured on the 50%, 12% and 3% concentrations. All measurements were made using electrodes. Sample salinity was calculated from the conductivity and temperature data. Un-ionized ammonia (NH_3) concentration was calculated from the total ammonia, pH, salinity, and temperature data.

For each experiment, SCCWRP attempted to calculate an EC_{50} (concentration producing a 50% reduction in fertilization) and NOEC (highest test concentration that does not produce a statistically significant reduction in fertilization). The EC_{50} was calculated by probit analysis of the raw percent fertilized data. If there was less than a 50% reduction in fertilization success, then an EC_{50} could not be calculated. The NOEC was calculated by first arcsine transforming the percent fertilized data, then subjecting it a one way analysis of variance (ANOVA). If a

significant difference between treatments was detected (p(0.05), a Dunnett's multiple range test was performed to test for differences between the control value and each of the concentrations. If there was not a significant reduction in fertilization relative to the control, then a NOEC could not be calculated.

3.4.2 Wet Weather Methods

Sampling was conducted during wet weather flow conditions at the Los Angeles and San Gabriel Rivers. Samples were taken during two storms for both the Los Angeles River and the San Gabriel River. The wet weather samples were collected by autosampler from the San Gabriel River on November 8, 1998 and January 26, 1999. A single grab sample was taken from the Los Angeles River during storms on March 15 and March 20, 1999. Sampling locations were LACDPW mass emission stations S-10 (Los Angeles River) and S-14 (San Gabriel River). Samples were stored under refrigeration until tested on November 11, 1998; and January 27, March 16, and March 22, 1999, respectively.

The wet weather toxicity tests were performed in the same manner as the dry weather toxicity tests discussed in the previous subsection.

Water quality measurements (pH, dissolved oxygen, conductivity, and total ammonia) were made on the test samples at the beginning of the toxicity test. For the river samples, water quality was measured on the 50%, 12% and 3% concentrations. All measurements were made using electrodes. Sample salinity was calculated from the conductivity and temperature data. Un-ionized ammonia (NH_3) concentration was calculated from the total ammonia, pH, salinity, and temperature data.

For each experiment, SCCWRP attempted to calculate an EC_{50} (concentration producing a 50% reduction in fertilization) and NOEC (highest test concentration that does not produce a statistically significant reduction in fertilization). The EC_{50} was calculated by probit analysis of the raw percent fertilized data. If there was less than a 50% reduction in fertilization success, then an EC_{50} could not be calculated. The NOEC was calculated by first arcsine transforming the percent fertilized data, then testing for homogenity of variance and normal distribution of the data. Data that passed these tests were then subjected to a one way analysis of variance (ANOVA). If a significant difference between treatments was detected (p(0.05), a Dunnett's multiple range test was performed to test for differences between the control value and each of the concentrations. Data that did not pass the test for homogenity of variance and/or normal distribution were subjected to a non-parametric Steel's Many-One Rank test. If there was not a significant reduction in fertilization relative to the control, then a NOEC could not be calculated.